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High-field far-infrared magnetospectroscopy of cobaltite/manganites

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Abstract
We have previously established using far-infrared spectroscopy, in both transmission and reflection geometries, that the phonon modes for the cobaltite/manganites $A(Co_{1/2}Mn_{1/2})O_3$ (A = La, Nd, Dy, Ho and Yb) show a correlation with the onset of metamagnetism in this series, as determined by susceptibility data. The far-infrared spectra in magnetic fields to 17.5 T for A = La, Nd, Ho and Yb show features which are not fully understood. The application of high magnetic field yielded an unexpected result: only the end member of the series,Yb, exhibited a field-dependence in the far-infrared transmission measurements. If this field-dependent behaviour were directly related to the metamagnetism, one would expect at least the Ho compound in addition to exhibit it. We discuss our latest data on a new series of samples for A = Ce, Pr and Dy, in which no clear shift in line positions is observed.

Keywords: Cobaltite; Manganite; Far-Infrared; High-Field; Magnetospectroscopy

Introduction

Troyanchuk *et al.* (1997) found that the cobaltite/manganites with smaller ions (Gd, Tb, Dy, Y and Ho) on the A site of the cobaltite/manganites $A(Co_{1/2}Mn_{1/2})O_3$ were metamagnetic, while those with larger ions (La, Pr, Nd, Sm and Eu) were not.

Gao *et al.* (2001) subsequently examined the phonon spectra of cobaltite/manganites by far-infrared methods. It was found that the phonon energies changed systematically, the phonon modes split, and new phonon modes appeared, as the mass of the lanthanoid on the A site varied. This was correlated with the appearance of metamagnetism in the series as previously determined by Troyanchuk *et al.* (1997).

A study of the far-infrared spectra in strong external magnetic field (Lewis *et al.* 2004) showed little field dependence on the spectra for A = La, Nd or Ho, but a marked effect for A = Yb. If the effect observed for Yb was directly related to metamagnetism, it would be expected to be evident for the Ho compound also, but this was not the case.

To attempt to resolve this anomaly, we have examined a further series of samples, with A = Ce, Pr and Dy, in strong magnetic field. A summary of the results of the previous experiments is provided in Table 1.

Materials and Methods

The ceramic samples used in this study were prepared by sintering in the conventional way. The starting materials were mixed then sintered at 1100 °C. The material was then ground and re-sintered at 1150 °C. Samples were prepared for transmission measurements by crushing the re-sintered material and diluting with CsI then pelletizing the resultant mix. A range of dilutions was experimented with and the best results were obtained with about 0.5% material in the CsI carrier.

The spectroscopy was carried out using a Bruker 113 V rapid-scan Fourier spectrometer. The light was conducted from the spectrometer to the magnetic field centre by a light pipe. The magnetic field was provided by a superconducting solenoid. The magnetic field was parallel to the propagation direction of the light from the spectrometer (that is, Faraday geometry was employed). The light was nominally unpolarised. A Si bolometer was employed as the detector.

Results and Discussion

The results for $Dy(Co_{1/2}Mn_{1/2})O_3$ are shown in Figure 1. Spectra are given for no magnetic field, then in magnetic fields in 3 T steps to 18 T. The zero-field data may be compared to the zero-field transmission data for the Dy compound that appears as Figure 1(c) of Gao *et al.* (2001). The main features are identical. The four prominent absorption lines are attributed, in order of increasing energy, to the external, torsional, bending and stretching modes (see Figure 2 of Gao *et al.* (2001) and the related discussion for identification). The former data was taken in a different spectrometer, a Bomem DA3.26 rapid-scan interferometer with a DTGS detector. The present data shows artefacts (spikes) at 264 and 528 cm^{-1}, corresponding to electrical pick up at the line frequency and the second harmonic, respectively.

Table 1: **Overview of the scope and results of studies of lanthanoid cobaltite/manganites**

Atomic Number	Element	Troyanchuk *et al.* 1997 metamagnetic?	Gao *et al.* 2001 spectral splitting?	Lewis *et al.* 2004 magnetic field features?
57	La	No	No	No
58	Ce			
59	Pr	No		
60	Nd	No	No	No
61	Pm			
62	Sm	No		
63	Eu	No		
64	Gd	Yes		
65	Tb	Yes		
66	Dy	Yes	Yes	
67	Ho	Yes	Yes	No
68	Er			
69	Tm			
70	Yb		Yes	Yes
71	Lu			

With regard to the effect of the magnetic field shown in Figure 1, there appears to be an increase in transmission as field increases; however, this is an artefact due to the magnetoresistance effect of the field on the Si detector. What is notable by its absence is any shift in line position, or any splitting of the lines with magnetic field.

The effect of the magnetic field may be brought out most clearly by taking the ratio of the data at field with the data in the absence of field. This is presented for the $Dy(Co_{1/2}Mn_{1/2})O_3$ sample in Figure 2. The sharp spikes are due to water vapour lines that are incompletely ratioed out in dividing the spectrum at field to the spectrum in zero field. This figure may be compared with Figure 2 of Lewis *et al.* 2004, in which similar data is presented for the compounds for A = La, Nd, Ho and Yb. In contrast to the data for the Yb sample, but in agreement with the data for the La, Nd and Ho samples, little change is observed on the application of the magnetic field.

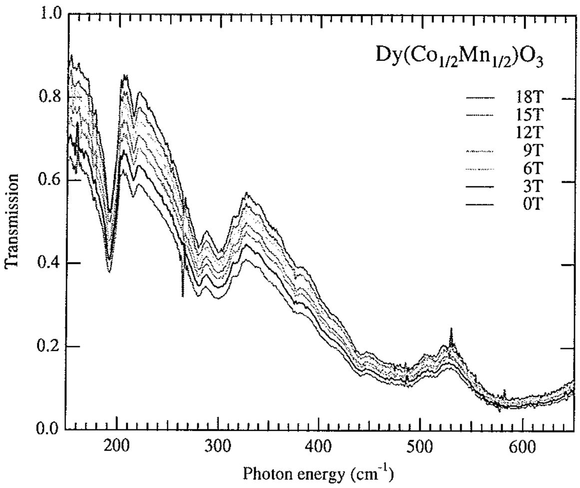

Figure 1: Far-infrared spectrum of $Dy(Co_{1/2}Mn_{1/2})O_3$ at magnetic fields of 18 (top), 15, 12, 9, 6, 3 and 0 (bottom) T.

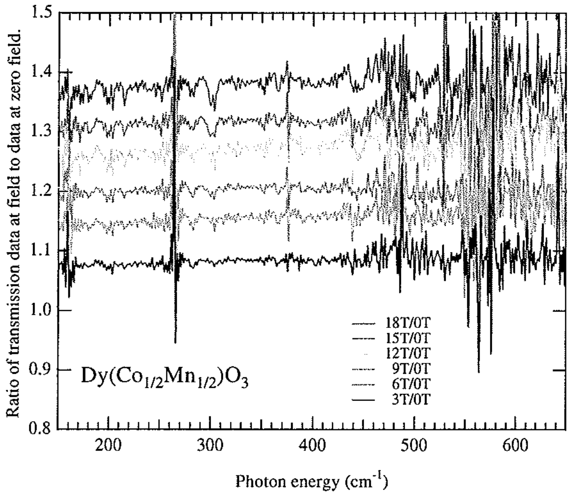

Figure 2: Far-infrared spectrum of $Dy(Co_{1/2}Mn_{1/2})O_3$ at field, ratioed with spectrum in zero field. Magnetic fields of 18 (top), 15, 12, 9, 6 and 3 (bottom) T.

Similar effects were observed for the compounds with A = Ce and Pr. There are shown as Figures 3 and 4, respectively.

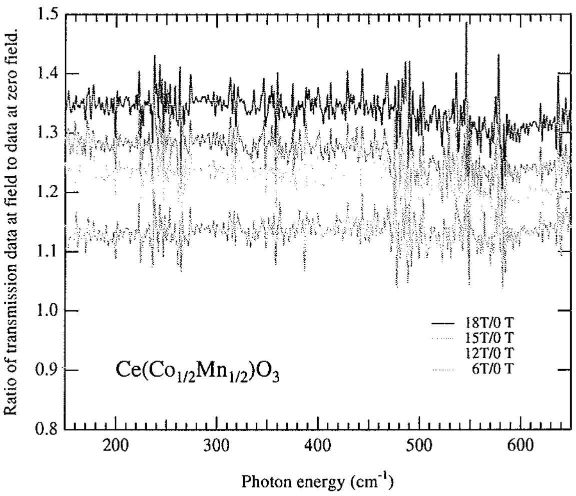

Figure 3: Far-infrared spectrum of $Ce(Co_{1/2}Mn_{1/2})O_3$ at field, ratioed with spectrum in zero field. Magnetic fields of 18 (top), 15, 12, and 6 (bottom) T.

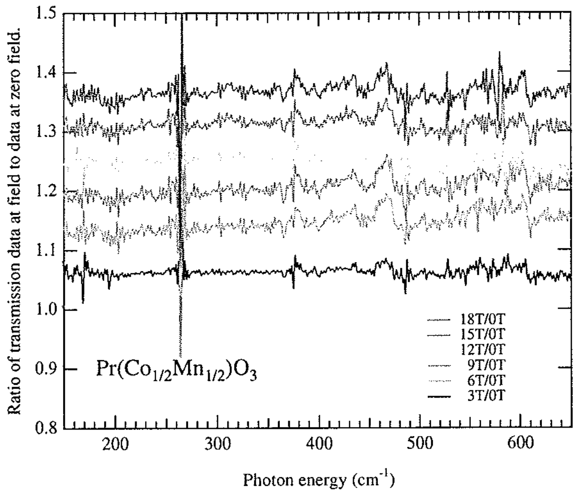

Figure 4: Far-infrared spectrum of $Pr(Co_{1/2}Mn_{1/2})O_3$ at field, ratioed with spectrum in zero field. Magnetic fields of 18 (top), 15, 12, 9, 6 and 3 (bottom) T.

In comparing the present results with the previous work, we have now found Ce and Pr, in addition to La and Nd studied previously, show little change in their spectrum as a result of the application of a magnetic field. None of these materials are expected to be metamagnetic.

We have examined three materials that Troyanchuk *et al.* (1997) would class as metamagnetic: $Dy(Co_{1/2}Mn_{1/2})O_3$, $Ho(Co_{1/2}Mn_{1/2})O_3$ and $Yb(Co_{1/2}Mn_{1/2})O_3$. Two of these (A = Dy and Ho) do not show a change in the far-infrared spectrum with magnetic field, whereas the other, A = Yb, does. We conclude that this magnetic field variation is not a property of metamagnetic materials *per se*, but seems to be related to Yb in particular. Further investigation is required to determine the microscopic origin of this behaviour.

Conclusions

We have found that $A(Co_{1/2}Mn_{1/2})O_3$ for A = Ce, Pr and Dy all show little change in their far-infrared spectra with magnetic field. Thus the effect observed previously in the A = Yb compound has not been seen in any other compound in this series, whether metamagnetic or not.

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